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[Second Edition.]

**PATENT SPECIFICATION****535,111***Convention Date (United States): Dec. 31, 1938.**Application Date (in United Kingdom): Nov. 22, 1939. No. 30580/39.**Complete Specification Accepted: March 28, 1941.***COMPLETE SPECIFICATION****An Improved Manufacture of Ethers from Olefins.**

We, STANDARD ALCOHOL COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at 26, Broadway, New York, New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The object of this invention is the production of ethers from olefins, particularly isopropyl ether from propylene by catalyzing the hydration of the olefin in a relatively weak solution of an acid capable of bringing about olefin hydration.

It is well known to saturate a concentrated acid absorbent with olefin to produce a reactive acid liquor comprising alkyl esters and unreacted acid; to dilute the reaction acid liquor with water to hydrolyze the esters forming a mixture of a very small amount of ether, alcohol and acid, holding mixture at elevated temperature to increase yield of ether, distil off the ether and alcohol and finally to separate the ether from the alcohol by fractionation. It is also known to circulate propylene gas through a body of acid liquor by which means a portion of the propylene is hydrated direct to ether and alcohol, the ether being removed from the catalytic body along with unreacted propylene from which the ether is recovered by condensation. The chief difficulty with the last described process is that, due to the vapor pressure of the ether, only a very limited amount of the olefin can be converted to ether per pass.

The catalytic material generally used for the formation of reactive acid liquors is sulphuric acid, although other catalytic materials can be used as, for example, phosphoric acid, hydrochloric acid and acetic acid, as can aqueous solutions of salts, such as zinc chloride and aluminium chloride, of concentration such as will form reactive acid liquors.

It is also known that when olefins are reacted with relatively dilute catalytic material, instead of a mixture of alkyl

esters and unreacted catalytic material being formed, alkyl esters, alcohols and ethers are formed, and after the lapse of a definite time the reaction attains an equilibrium. Instead of olefins and acid, alcohol and acid may be reacted to form the reactive acid liquor.

The process forming the subject of the present invention is of the kind wherein the olefinic gases are passed through a catalytic acid liquor such as a solution of sulphuric acid capable of reacting with olefins at an elevated temperature and pressure to form a reactive acid extract, ether being removed from the acid extract by distillation at a reduced pressure and at a temperature which may be similar to that of the absorption temperature. Such a process is described in prior Specification No. 403,654.

According to the present invention the acid extract is partially stripped by conducting it to a zone maintained at a temperature substantially equal to that of the olefin absorption zone but of a reduced and preferably a substantially atmospheric pressure where the ether is volatilized together with a small proportion of alcohol to form an ether-alcohol mixture and a partially stripped extract. The ether is separated from the alcohol, which is returned to the partially stripped extract and there is added to the extract an amount of water equal to that utilized in the production of the ether, whereupon the restored alcohol-containing extract is returned to the olefin absorption zone. By operating in this manner a high rate of conversion of olefin into ether per pass of the olefin is obtained.

In practising this invention, olefins are advantageously passed into an absorption tower containing a catalytic acid liquor such as has been previously described and maintained at a temperature and pressure that will cause a rapid hydration of the olefin. The olefin remaining unreacted after passing through the absorption tower is returned to the feed line for recycling through the absorption tower. The saturated extract is removed from the bottom of the absorption tower and passed into a flash stripping tower main-

tained at atmospheric pressure, the temperature of which is held within the limits 90°-105° C., preferably 95°-100° C. Here substantially all of the ether and small quantities of the alcohol and water are volatilized leaving an extract which contains practically all of the remaining olefin as alcohol or alkyl ester in the acid catalyst. The extract stripped of ether is then diluted with sufficient water to replace the water removed by the formation of ether and that taken overhead from the flash stripping still and is returned to the top of the absorption tower. In cases where pure ether is desired, the vaporous ether-alcohol mixture is removed from the flash tower and processed to separate the ether from the alcohol by methods well known to the art. This alcohol is then returned together with the stripped extract to the top of the absorption tower. The acid extract stripped of ether is more efficient in converting olefin to ether than if fresh catalyst were always fed into the top of the absorption tower.

The invention will be more fully understood when read with reference to the accompanying drawings, wherein

Fig. 1 shows a diagrammatic view in sectional elevation of an apparatus adapted to carry out the process of the invention using substantially pure olefin as the feed gas, and indicates the flow of materials, and,

Fig. 2 shows a similar view wherein a mixture of saturated and unsaturated hydrocarbons is used as the feed gas.

Referring to Fig. 1, numeral 1 represents a feed pipe carrying substantially pure olefin to the bottom of absorption tower 2. The absorption tower may be of any conventional type to hold the absorption medium, either plate or packed, and is maintained at a temperature above 30° C., preferably 80°-120° C., and at a pressure above 2 lbs. gauge pressure (corresponding to the minimum temperature of 30° C.), preferably 150-200 lbs., to give a rapid hydration reaction with the hydration catalyst. Any unabsorbed olefin is removed from the top of the tower through line 3 and returned to the bottom of the tower through feed line 1. For purposes of illustration, tower 2 is filled with sulphuric acid of less than 84% strength, preferably 50% to 70%, although dilute solutions of any of the previously enumerated catalysts might be used. The absorption medium and the olefin react to form a reactive acid extract which is a mixture of olefin, acid, ether, alcohol and alkyl ester. This extract is withdrawn from tower 2 through line 4 and

conducted to tower 5. Tower 5 is a stripping still of the film heater type, for example, a packed tower. The saturated extract entering tower 5 through line 4 is allowed to flow down the tower and ether and small amounts of alcohol are vaporized off the top. About 15% of the ether-alcohol mixture leaving tower 5 is alcohol when operating under preferred absorption conditions. The ether-alcohol mixture is conducted through line 6 to an ether-alcohol separator 9. The partially stripped reactive acid extract is removed from tower 5 through line 7, sufficient water to make up that used in the formation of ether is added through line 8 and the extract is returned to the top of tower 2. The alcohol recovered from the ether-alcohol separator 9 is returned through line 11 to line 7 and thus to the top of the absorption tower.

The disclosure in the preceding paragraph concerns an apparatus and process adapted to convert substantially pure olefins to ether. Substantially pure olefins, however, are not always available, and it has been found that with very little modification the same principles utilized in converting substantially pure olefin to ether may be utilized in converting the olefin in a mixture of gases to ether. In Fig. 2, numeral 12 represents the incoming feed line carrying a mixture of gases to the bottom of absorption tower 13. Absorption tower 13 corresponds in all respects to the absorption tower 2 of Fig. 1 described above. Numeral 14 represents the line by which waste gases are removed from absorption tower 13. Flash tower 16 corresponds to tower 5 of Fig. 1 and functions accordingly as described above. Lines 15 and 17 of Fig. 2 correspond to lines 4 and 6 of Fig. 1 and function similarly. The partially stripped extract is withdrawn from tower 16 through line 21 where it is divided, a major part flowing through line 23 and the remainder through line 23. The flow through line 22 is augmented by the condensed alcohol from the ether-alcohol separator 18 and stripping still 25, sufficient water is added through line 24 to replace the water used in the formation of ether and the whole is returned to a point midway of the absorption tower 13. The partially stripped extract flowing through line 23 is conducted to a place near the top of the tower 25. Tower 25 is a stripping still of either the open steam or heated coil type. In still 25 the partially stripped extract is completely stripped of all alcohol which is taken off through line 26, condensed in condenser 27 and returned to the system through line 22.

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The completely stripped acid is removed from still 25 through line 28, reconditioned, if necessary, in a concentrator (not shown) and returned to the top of absorption tower 13. By operating in this manner, full advantage is taken of the principle of flashing off the ether from the acid extract without loss of olefin because the fresh acid entering the top of tower 13 removes substantially all of olefin from the gas taken off through line 14.

## EXAMPLE:

500 cc's of 60%  $H_2SO_4$  were charged to an absorber and brought to 100° C. Substantially pure propylene was then passed through the acid for a period of one hour, the pressure being maintained at 190 lbs. gauge. At the end of the hour there was obtained 1050 cc's of reactive acid liquor. Upon analysis, (that is, by dilution with  $H_2O$  followed by distillation) 200 cc's of this extract gave 32 cc's isopropyl ether and 111 cc's of alcohol. The remaining 850 cc's of extract was flash stripped at 95°-100° C. and atmospheric pressure, giving as a distillate 105 cc's of di-isopropyl ether, 21 cc's of isopropyl alcohol and water. This corresponds to a recovery of ether of 77%. The stripped extract was analyzed and found to contain 4.5 cc's ether and 64.5 cc's alcohol per 100 cc's of extract.

520 cc's of the stripped extract, together with 15 cc's of water, were charged back to the absorber and permitted to react with propylene for one hour at 100° C. and 190 lbs./sq. in. pressure. An analysis of this extract gave 74.5 cc's of ether and 335.5 cc's of alcohol in the extract. At the rate of 4.5 cc's ether per 100 cc's extract charged, there were charged to the absorber 24 cc's of ether. There was obtained from the extract 74.5 cc's of ether or a total of 50.5 cc's ether over that charged. Based upon the 64.5 cc's per 100 cc's of extract, there were charged to the absorber 334 cc's of alcohol. The extract, after reaction with propylene for one hour, yielded 335.5 cc's alcohol showing the formation of only 1.5 cc's of alcohol.

The 520 cc's of stripped extract charged to the absorber as described above contain 3.22 mols of  $H_2SO_4$ . Another run was made using 2.22 mols of  $H_2SO_4$  in the form of 60% fresh acid, absorbing propylene for one hour at 100° C. and 190 lbs./sq. in. pressure. This run yielded only 23 cc's of isopropyl ether which is a materially reduced yield when compared with the 50.5 cc's of ether formed when stripped extract was used as the absorption medium.

The preceding specification, and the

data showing the results obtained by the use of the present invention, show its character and value over present practice but they are for illustrative purposes only and are not to be construed as imposing undue limitations upon the claims which are to be construed as broadly as the prior art will permit.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of ether from a substantially pure olefin or from gases containing olefins, which comprises passing the gases through a catalytic acid liquor capable of reacting with olefines to form a reactive acid extract, said acid liquor being maintained at a temperature above 30° C. and at a correspondingly elevated pressure above 2 lbs. per sq. in. gauge pressure, such as to cause rapid hydration of the olefin, conducting the acid extract to a zone maintained at a temperature substantially equal to that of the absorption zone but at a reduced and preferably atmospheric pressure where the ether in the reactive acid extract is volatilized together with a small proportion of the alcohol to form an ether-alcohol mixture and a partially stripped extract, separating the ether from the alcohol and returning alcohol to the partially stripped extract, restoring the extract by replenishing the water in the extract utilized in the production of ether and returning restored alcohol-containing extract to the absorption zone.

2. A process as claimed in Claim 1, wherein the catalytic acid liquor for reacting with olefine to form a reactive acid extract is sulphuric acid of less than 84% concentration and preferably from 50% to 70%.

3. A process as claimed in Claim 2 for the production of isopropyl ether from gases containing propylene, wherein the gases are passed through 60% sulphuric acid in an absorption zone to form the reactive acid extract, said sulphuric acid being maintained at 100° C. and at a pressure above 72 lbs. per sq. in.

4. A process as claimed in any of Claims 1 to 3, wherein the restored extract is returned to the absorption zone at a point above the incoming gas inlet.

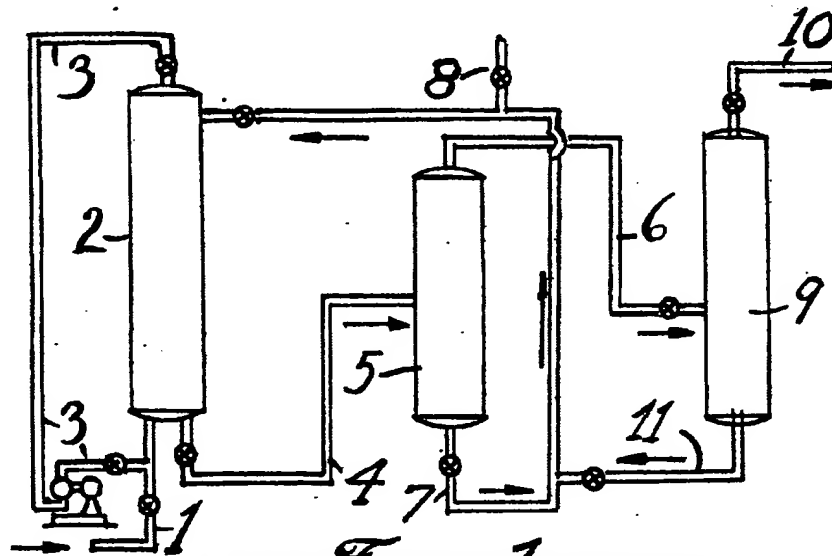
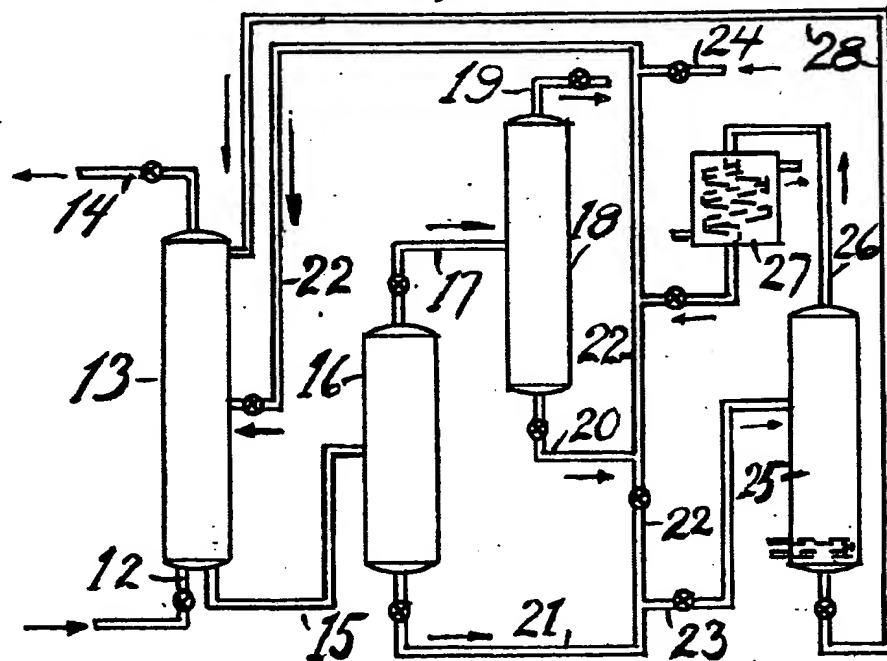
5. A process for producing isopropyl ether according to Claim 3 or to Claim 4, in which the partially stripped extract from the low pressure zone is divided into two portions, preferably into a major and a minor portion, the minor portion being completely stripped of alcohol and other olefin hydration products, e.g. esters,

## 535,111 COMPLETE SPECIFICATION

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[This Drawing is a reproduction of the Original on a reduced scale.]

Fig-1Fig-2

H.M.S.O. (ty.P.)